

Water Rock Interaction [WRI 14]

Nitrogen changes between rural and peri-urban stream subsurface waters (Yzeron stream, France)

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Abstract

Urbanization subjects stream and groundwater to increased loads of organic nitrogen, nitrate, and ammonium. Therefore, studying nitrogen species at the urban stream-aquifer interface is important for water resource management. We report here results on water $^{18}\text{O}/^{16}\text{O}$ ratios and on nitrogen species in stream subsurface waters upstream and downstream of several combined sewer overflows (CSOs) in a rural area and peri-urban area, respectively. Water $^{18}\text{O}/^{16}\text{O}$ ratios were measured to trace the mixing of subsurface waters with stream channel water. Organic nitrogen (ON) and carbon (OC) slightly increased between rural and peri-urban environments in the cold season, but not in the warm season. The highest nitrate levels were observed in rural subsurface waters in the cold season. The lowest nitrate levels were found in peri-urban subsurface waters in the warm season; they corresponded to slow exchange of subsurface waters with channel water.

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1. Introduction

The fate of the organic and inorganic nitrogen loaded in streams depends on the retention and transformation processes in stream surface and subsurface waters. An important zone for N retention and

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transformation in streams is the stream-aquifer interface. It corresponds to the zone below the streambed in which water exchanges occur between the open channel and subsurface waters and has been shown to be of critical importance for N redox reactions in streams [1]. A key process controlling the distribution of dissolved O_2 and nitrogen species in stream subsurface waters is the inflow of channel water into the streambed and its mixing with subsurface waters [1-4]. Despite its importance for N transformations, the interface between surface and subsurface waters remains under-investigated in urban streams. Data on the impact of urban inputs on nitrogen species at the stream-aquifer interface are thus needed.

In the present study, we investigated the changes in the forms of nitrogen (organic nitrogen, NO_3^- , NH_4^+) between rural and periurban subsurface waters of a stream (Yzeron, France). The rural and periurban locations studied were located respectively upstream and downstream from several combined sewer overflows (CSOs) (Fig. 1). The specific questions addressed were: (i) Does the extent of mixing subsurface waters with surface water, as revealed by oxygen isotopes, differ between rural and peri-urban environments? (ii) Does the organic nitrogen content of fine sediments and subsurface waters differ between the two environments? (iii) Do organic nitrogen and biodegradable organic matter content and/or mixing with surface water affect dissolved O_2 and nitrate in stream subsurface waters?

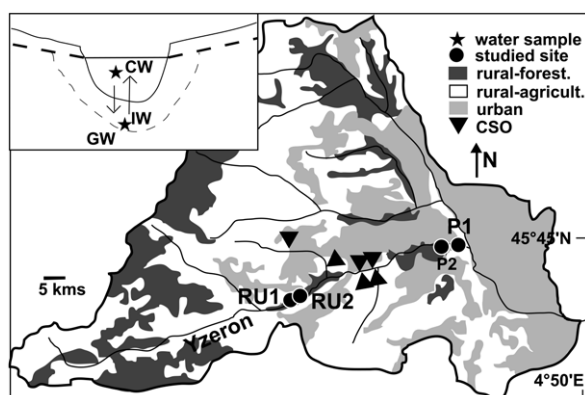


Fig. 1. Map of the Yzeron basin showing the CSOs, the rural (RU1, RU2) and periurban (P1, P2) locations studied. In this granitic-gneissic basin, groundwater is limited to an aquifer in colluvial and stream alluvial deposits. The inset schematically represents the relationship between the channel (CW) and groundwater (GW) components in the interstitial waters (IW) studied. The IWs were taken at a depth of fifty centimetres below the streambed surface.

2. Exchange of interstitial with channel waters: oxygen isotope constraints

Water oxygen isotope composition was used to characterize channel (surface) and interstitial (subsurface) waters and evaluate the extent of mixing of interstitial waters with channel water. In June 2004, the sampling was performed 9-11 hours after a storm event. The stream channel was richer in heavy isotopes compared to pre-storm channel waters (ps) (Fig. 2). Peri-urban interstitial waters (-8.5 to -7.8‰; Fig. 2b) kept pre-storm values, thus presenting slight mixing with “new” channel water at a timescale of 9-11 hours. In contrast, the $\delta^{18}O$ value of rural interstitial waters rose (Fig. 2a) approaching that of channel water. A simple oxygen isotope mass balance was used to estimate the fraction of “new” channel water in interstitial waters (f_{renewed}). This fraction of “new” channel water in interstitial waters ranged from 0.21 to 1 in the rural reach (with a mean of 0.5) and from 0 to 0.20 in the peri-urban one (with a mean of 0.1). The most rapid exchange was found in the upstream part of the rural riffles with (f_{renewed} between 0.82 and 1) while the slowest exchange was in the downstream end of the peri-urban riffles (f_{renewed} down to 0). In November 2004, the values of rural interstitial waters fell between that of channel water and values that are richer in ^{18}O . The ^{18}O -rich end member (Fig. 2a) can be related to groundwater

derived from summer rains. The fact that interstitial waters differed significantly from channel water indicated less efficient exchange between channel and interstitial waters (compared to June 2004). In contrast most peri-urban interstitial waters matched channel water in November 2004, indicating that peri-urban channel and interstitial waters had similar isotopic signatures and/or that interstitial waters were fed by channel water (Fig. 2b). When considering chemical data (nitrate, dissolved O_2 , DIC), the values of most peri-urban waters fell close to those of channel waters in the cold season (November 2004, February 2005) (Fig. 2b), suggesting infiltration of channel water into the streambed sediments.

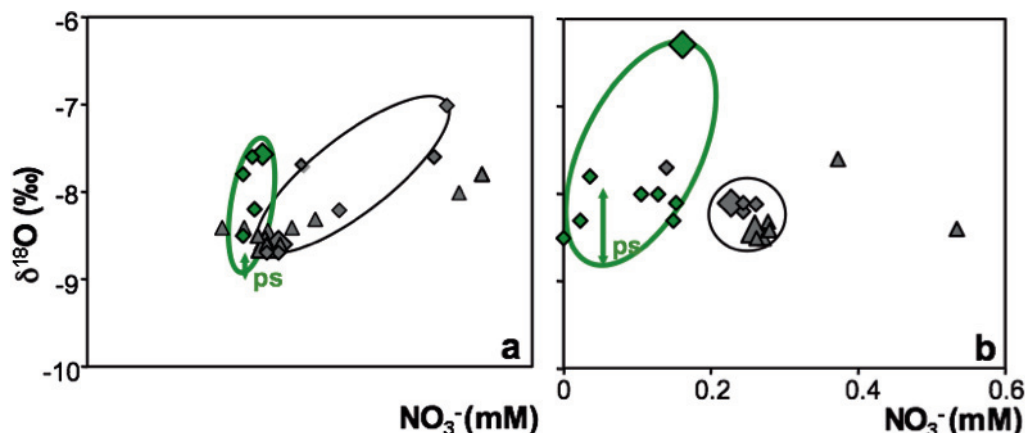


Fig. 2. Water $\delta^{18}O$ values versus nitrate concentrations in the waters of the rural (a) and peri-urban (b) Yzeron stream. Large and small symbols represent the channel and subsurface waters, respectively. The green outlined area shows the samples collected in June 2004 (green diamonds), the ps bar the $\delta^{18}O$ range of pre-storm interstitial waters. The black outlined area shows the samples collected in November 2004 (grey diamonds). Grey triangles represent the samples from February 2005.

3. Addition of organic nitrogen in the peri-urban sediments and interstitial waters

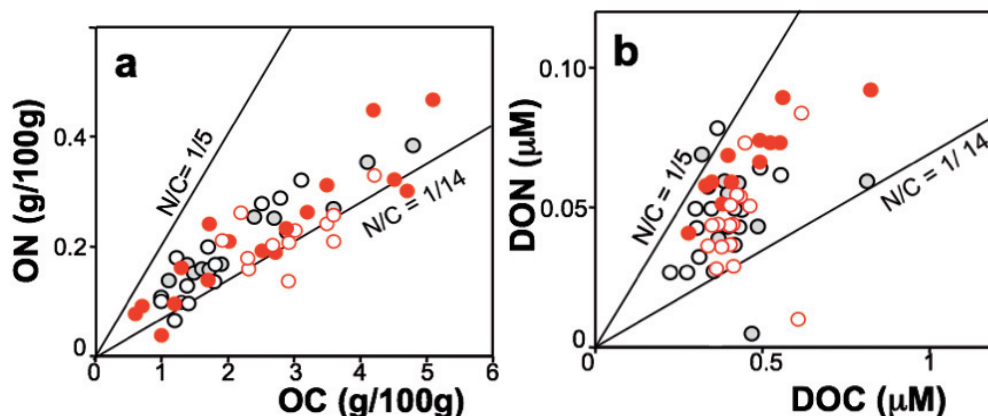


Fig. 3. (a) Organic nitrogen (ON) versus organic carbon (OC) content of fine sediments; (b) Dissolved organic nitrogen (DON) versus dissolved organic carbon (DOC) of subsurface waters. Open and filled symbols represent samples collected in the warm period (June 2004, June 2005) and cold (November 2004, February 2005) seasons, respectively. Black and red symbols represent rural and peri-urban samples, respectively.

The peri-urban fine sediments of Yzeron stream had a higher OC content ($p < 0.05$) (3.12 ± 1.11 g/100g, $n = 16$) than the rural ones (2.17 ± 1.15 g/100g, $n = 15$). The DON increased significantly ($p < 0.01$) during the cold season from rural (0.054 ± 0.008 mM, $n = 19$) to peri-urban interstitial waters (0.064 ± 0.014 mM, $n = 17$), but not in the warm season (Fig. 3).

The slight increase in ON and OC between rural and peri-urban samples is consistent with organic-matter-rich inputs to the peri-urban environment, possibly from CSOs. In the warm season, the decrease in peri-urban DON indicates a negative balance between ON input and loss at that time of the year, likely related to enhanced DON biodegradation.

4. Spatial and temporal patterns of nitrate

Nitrate, the dominant dissolved inorganic nitrogen species in both channel and interstitial waters, varied by two orders of magnitude in interstitial waters (0.005 to 0.55 mM) (Fig. 2). We observed that under low flow (June 2004), water $^{18}\text{O}/^{16}\text{O}$ ratios showed high renewal of rural interstitial waters with channel water while interstitial water had a nitrate content similar to that of surface water (Fig. 2) and remained oxic (data not shown). There was little if any apparent removal of nitrate from subsurface waters, probably because of high exchange between subsurface and surface waters. Under higher flow (November 2004), rural interstitial waters with high nitrate levels had $^{18}\text{O}/^{16}\text{O}$ fingerprints of local groundwater and should be derived from shallow flow paths on adjacent hill slopes. The high nitrate concentration of these waters can therefore be related to nitrate leaching from adjacent rural areas.

A seasonal change of nitrate was also found in peri-urban waters. However, although the channel of both rural and peri-urban reaches had high nitrate concentrations (0.16 to 0.26 mM), they presented different nitrate patterns in the interstitial waters. In the cold season, under high flow, water $^{18}\text{O}/^{16}\text{O}$ ratio, nitrate (Fig. 2), dissolved O_2 and DIC (not shown here) indicated that channel water infiltrated into the peri-urban streambed. By contrast, the rural subsurface waters showed increased groundwater contribution and decreased exchange with channel water (compared to the warm season). The isotopic and chemical data thus suggested that in the cold season the channel is recharged by groundwater in the rural area and that it discharged into the peri-urban stream aquifer. The high nitrate level of peri-urban interstitial waters in that period of the year was thus partly related to nitrate moving from upstream.

In the warm season, a clear decrease in nitrate was found in peri-urban subsurface waters but not in the rural ones. This corresponded to lower renewal of interstitial waters by channel water in the peri-urban environment. Indeed, the interstitial waters of peri-urban subsurface waters showed slower renewal than the rural ones in June 2004, as shown by the $^{18}\text{O}/^{16}\text{O}$ data. Lower renewal was observed in the downstream part of riffles where interstitial waters had the longest residence time in bed sediments and presented the highest nitrate loss. Therefore slow exchange between subsurface and surface waters and enhanced inputs of organic matter seemed to favor nitrate reduction in the downstream, peri-urban, subsurface waters impacted by CSOs.

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